

平成16年登簿第

認

証



7/15 号

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よって、これを認証する。

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証

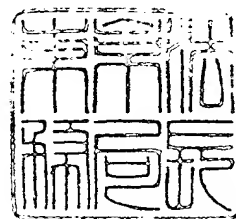
明

上記署名は、東京法務局所属公証人の署名に相違ないものであり、かつ、その押印は、  
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平成16年 5 月 12 日

東京法務局長

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### APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: JAPAN

This public document

2. has been signed by TOICHI FUJIWARA

3. acting in the capacity of Notary of the Tokyo Legal Affairs Bureau

4. bears the seal/stamp of TOICHI FUJIWARA

Certified

5. at Tokyo

6. MAY 12 2004

7. by the Ministry of Foreign Affairs

8. 04- № 002446

9. Seal/stamp:

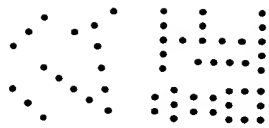
10. Signature



*S. Hagiwara*

Shinichi HAGIWARA

For the Minister for Foreign Affairs



Registration No. 715

DECLARATION

I, Yuki MIYAKE residing at 1223-1 A-409, Sonno-cho, Inage-ku, Chiba-shi, Chiba, 263-0051, Japan do hereby solemnly and sincerely declare:

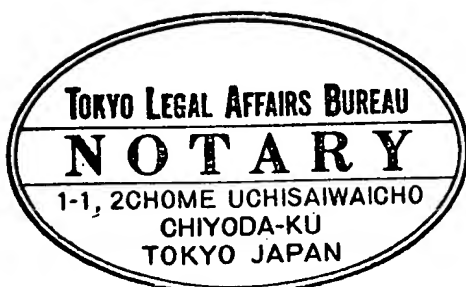
1. That I am an employee of Furuya & Co. located  
at Hamacho-Hanacho Building, 2-17-8, Nihonbashi-Hamacho, Chuo-ku,  
Tokyo 103-0007, Japan,
2. That I am well acquainted with the Japanese and English  
languages, and
- 三宅有紀 3. That the attached English document is a true and correct translation into  
English of the certified copy of the Japanese patent application No. 6-  
318547 filed on 21 December 1994, a copy of which is hereto attached.

And I make this solemn declaration conscientiously  
believing the same to be true and correct.

on the date of 12 May 2004

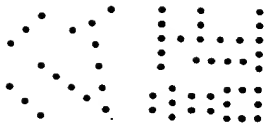
三宅有紀

By Yuki MIYAKE  
This is to certify that this document  
was subscribed before me by the above-named  
person(s) on this day.



MAY 12 2004

*Toichi Fujiwara*  
TOICHI FUJIWARA  
NOTARY



Patent Office  
Japanese Government

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application: 21 December 1994

Application Number: patent application No. 6-318547

Applicant(s): Daicel Chemical Industries, Ltd.

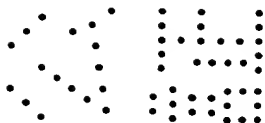
dated 5 January 1996

Commissioner

Patent Office

Mr. Yuji KIIYOKAWA

Shusho No.  
Shushotokuhei 07-3078264



[Designation of Document] Patent Application

[Reference Number] 194DK102

[Application Date] 21 December 1994

[Addressee] the Commissioner of the Patent Office

[IPC] C06D 5/06

[Title of the Invention] Gas Generant Composition

[Number of Claims] 7

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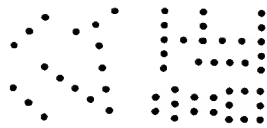
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[Designation of the Payment]

[Way of Payment] prepayment

[Number of the Deposit] 010685

[Amount of the Payment] 21,000

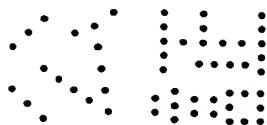
[List of the Exhibit]

[Name of the Subject] Specification 1

[Name of the Subject] Abstract 1

[Number of the General Power of Attorney] 9005922

[Request of the proof] yes



JP6-318547

[Designation of Document] Specification

[Title of the Invention] Gas Generant Composition

[Claims]

[Claim 1] A gas generant composition having, as the essential components, a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer, which comprises manganese dioxide having a specific surface area of not less than 50 m<sup>2</sup>/g.

[Claim 2] The composition according to claim 1, wherein the nitrogen-containing organic compound is at least one selected from the group consisting of organic compounds containing amino group or amido group and tetrazole derivatives.

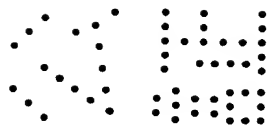
[Claim 3] The gas generant composition according to claim 2, wherein the organic compound containing amino group or amido group is azodicarbonamide.

[Claim 4] The gas generant composition according to claim 2, wherein the tetrazole derivative is aminotetrazole.

[Claim 5] The gas generant composition according to claim 1, wherein the oxygen-containing inorganic oxidizer is at least one selected from the group consisting of KNO<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>2</sub> and KClO<sub>4</sub>.

[Claim 6] The gas generant composition according to claim 1, wherein the oxygen-containing inorganic oxidizer is KClO<sub>4</sub>.

[Claim 7] The gas generant composition according to claim 1,



wherein the nitrogen-containing organic compound is azodicarbonamide and the oxygen-containing inorganic oxidizer is  $\text{KClO}_4$ .

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

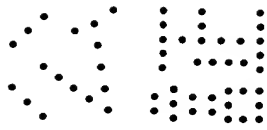
The present invention relates to a gas generant composition. More specifically, the invention relates to a non-azide type gas generator composition which supplies gas components by burning for the purpose of inflating an air bag system.

[0002]

[Prior Art]

In the event of collision of vehicles like cars at high speed, the driver and passengers might be injured or killed by clashing against internal hard or dangerous parts of the vehicles such as the handle and front glass. In order to prevent such disasters, air bag systems for automobiles have been developed which inflate quickly by a gas generated from a gas generant.

Requirements for the gas generant of an automobile air bag system are very severe. At first, the bag should inflate in a very short period of time, usually not longer than 40 to 50 milliseconds. Further, The atmosphere within the bag is most suitable when it corresponds to the air composition in the car. These requirements are satisfied by gas generants which have been currently used in common

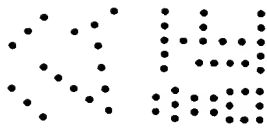


comprising a base gas generant such as alkali metal salts (in particular sodium azide) or alkaline earth metal salts of hydrazoic acid. However, these gas generants are seriously defective in that the main component, sodium azide is toxic and that the by-products alkali components are also toxic. Hence, environmental pollution brought by a large amount of scrap cars and health hazard of the driver and passengers when the gas is generated are concerned.

[0003]

For the purpose of overcoming these problems, non-azide type gas generants have been under development in place of sodium azide type. For example, JP-A 3-208878 discloses a composition which comprises a main component of oxygen-containing oxidizer such as tetrazole, triazole, or their metal salts combined with ammonium perchlorate or sodium nitrate and an auxiliary component of a metal oxide such as  $V_2O_5$ ,  $CuO$  or  $Fe_2O_3$ . The metal oxide mentioned forms a solid combustion product, which is easily removed by filtration when undesired components are removed by filtration prior to release the formed gas into the bag in an air bag system, and converts CO which is toxic to human bodies generated from the nitrogen-containing organic compound to  $CO_2$ . JP-B 64-6156 and JP-B 64-6157 disclose a gas generant which contains, as the main component, a metal salt of bitetrazole compound that does not contain hydrogen. JP-A 3-208878 further discloses a gas generant having a transition metal complex of aminoarazole as the main component. These non-azide type





compounds disclosed in the series of prior art references are characteristic in that the concentration of carbon monoxide released is low since the carbon number in the one molecule is small; however, the amount of nitrogen oxides, toxic to human bodies, increases in all the cases and the performance is not satisfactory in respect of the inflation period of the bag.

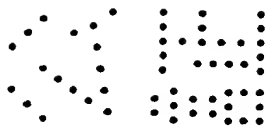
[0004]

[Problem to be Solved by the Invention]

The present inventors previously had found that a non-azide type gas generant having a nitrogen-containing organic compound such as azodicarbonamide and a certain inorganic oxygen-containing oxidizer as the effective component is free from environmental pollution, satisfactory in respect of the inflation period of the bag, and advantageous in the cost, and filed the patent applications (with reference of JP-A 4-185251, JP-A 4-185253 and JP-A 5-18782).

[0005]

In the combustion of an organic compound containing oxygen, it is well-known that carbon monoxide will generate as incomplete combustion product even when an oxidizer is used in an amount exceeding the chemical equivalence that releases the necessary amount of oxygen for burning combustible elements, such as carbon, hydrogen and others, in the organic compound. In view of this fact, the nitrogen compound, such as azodicarbonamide, used as the main agent in the mentioned



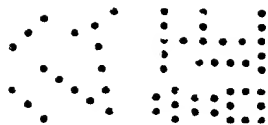
gas generant is supposed to release a relatively rather large amount of carbon monoxide and nitrogen oxides, and a trace of NO<sub>x</sub> which contains a little amount of nitrogen is produced as a by-product since many carbon atoms are contained per molecule. For the purpose of avoiding such by-product carbon monoxide, use of a catalyst may be possible which convert carbon monoxide to carbon dioxide. Many components are known for such catalysts as written in a book "Classified Table for Catalysts depending on Reaction, Vol. I" edited by Tarama et al. of Kyoto University and published by Kagaku Kogyo-sha (see pp. 291-292). However, no catalysts are known that are generally reactive enough in a contact period of time of several dozens milliseconds as required for a gas generant for air bag system; V<sub>2</sub>O<sub>5</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub>, and other metal oxides are used at present in spite of their low activity. And, such a catalyst that decomposes NO<sub>x</sub> without a reducing agent is hardly known.

[0006]

[Means to Solve the Problem]

The present inventors have intensively studied for overcoming the problems mentioned above and have found, surprisingly, that manganese dioxide having a certain physical property has an important function for decreasing carbon monoxide and nitrogen oxides; this finding has lead to completion of a first embodiment of the present invention.

According to the present invention, a gas generant composition containing a nitrogen-containing organic compound and an oxygen-



containing inorganic oxidizer as the essential components is provided, which composition is characterized by containing manganese dioxide having a specific surface area not less than 50 m<sup>2</sup>/g.

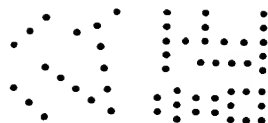
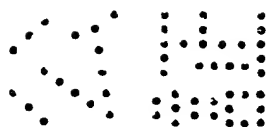
[0007]

The gas generant composition of the present invention contains a nitrogen-containing organic compound and a oxygen-containing inorganic oxidizer as the essential components.

There is no particular limitation for the nitrogen-containing organic compound usable for the present invention provided that nitrogen atom is contained in the molecule; examples of the nitrogen-containing organic compound include organic compounds containing amino group or amido group and tetrazole derivatives. Specific examples of the organic compounds containing amino group or amido group include: azodicarbonamide, urea, aminoguanidine bicarbonate, biuret, dicyandiamide, and hydrazides; preferably azodicarbonamide. Specific examples of the tetrazole derivatives include: aminotetrazole, tetrazole, azotetrazole, bitetrazole, tetrazole carboxylate, their alkali metal salts and their alkaline earth metal salts; and preferably aminotetrazole. The nitrogen-containing organic compound may be used in single or as a mixture of two or more kinds.

[0008]

The oxygen-containing inorganic oxidizer usable in the present invention may be selected widely from known ones such as nitrates,

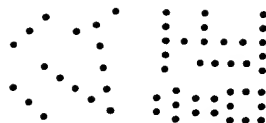


nitrites, and oxyhalogenates. Specific examples of the oxygen-containing inorganic oxidizer include potassium nitrate, sodium nitrate, strontium nitrate, potassium nitrite, sodium nitrite, sodium perchlorate, potassium perchlorate, sodium chlorate, and potassium chlorate. More specifically, a single compound or mixture selected from  $\text{KNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ , and  $\text{KClO}_4$  may be used;  $\text{KClO}_4$  is preferable in particular.

[0009]

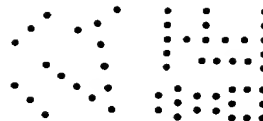
The blend ratio of the nitrogen-containing organic compound to oxygen-containing inorganic oxidizer in the gas generant composition of the present invention may be optionally selected depending on the combustion rate, combustion temperature and combustion temperature, although the ratio is normally selected so as to be stoichiometric when the nitrogen-containing organic compound is completely oxidized and burned on the basis of the oxygen amount. For example, about 20 through 400 parts by weight of the oxygen-containing inorganic oxidizer is blended with 100 parts by weight of the nitrogen-containing organic compound; blending some excess amount of the oxygen-containing inorganic oxidizer compared to the stoichiometric amount for complete combustion is preferred for enhancing the efficiency of oxidizer catalyst provided that the gas generation efficiency based on the unit weight of the gas generant composition is not substantially lowered.

[0010]



According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, manganese dioxide having a specific surface area not less than  $50 \text{ m}^2/\text{g}$ , preferably  $100\text{-}300 \text{ m}^2/\text{g}$ , is further blended as the oxidation catalyst. Use of manganese dioxide of specific surface area less than  $50 \text{ m}^2/\text{g}$  does not bring the effect of decreasing carbon monoxide and nitrogen oxides in the generated gas.

The manganese dioxide can be produced by a process known to the art. For example, a process described in a book "Genso Betsu Shokubai Binran (Handbook of Catalysts Classified by Elements)" edited by Catalysis Society of Japan and published by Chijinshokan Co., Ltd. (in Page 411-412) or a process disclosed in DE 1,593,320 or in JP-A 3-68447 may be adopted; in order to get the manganese dioxide having a specific surface area not less than  $50 \text{ m}^2/\text{g}$ , drying the prepared manganese dioxide at a temperature not higher than  $200^\circ\text{C}$  is preferable. Higher drying temperature is not desirable because it will decrease the surface area and lower the activity due to reduction of a part of the manganese dioxide. While the manganese dioxide usable in the present invention is obtained by the mentioned process, the preparation process is not limited specifically as long as the specific surface area is not less than  $50 \text{ m}^2/\text{g}$ . The particle size of manganese dioxide is not limited specifically as well; however, fine powder such as  $0.5 \mu$  or less is not preferable because of excessive



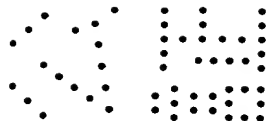
load for the filter in filtration step.

[0011]

In the present invention, the content of manganese dioxide is not limited, but normally 1 through 30% by weight, preferably 3 through 20% by weight, and more preferably 3 through 10% by weight, of the total weight of the composition that includes the gas generant composition containing the nitrogen-containing organic compound and oxygen-containing inorganic oxidizer as the essential components and a third component to be blended in some cases. Too much manganese dioxide content is not desirable because the amount of generated gas is decreased against unit weight of the gas generant composition; and too little content is not desirable because the effect of decreasing toxic gas concentration is unsatisfactory.

[0012]

For the purpose of enhancing the shaped strength of the gas generant composition, a binder, a decomposition promoter of nitrogen-containing organic compound, silica or the like may be blended. Examples of the binder include: fine crystal binders such as marketed under the trade name "Avicel"; polymer binders such as poval; organic binders such as starch. As a decomposition promoter of nitrogen-containing organic compound, an oxide decomposition promoter or an organic decomposition promoter can be used. Examples of an oxide decomposition promoter are, specifically, CuO, ZnO, ZnCO<sub>3</sub>, FeCl<sub>3</sub>, Pd<sub>3</sub>O<sub>4</sub>, PdO<sub>2</sub>, PdO, Sb<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, CeO<sub>2</sub>, Ba<sub>2</sub>O<sub>3</sub>, CaO<sub>2</sub>, YbO<sub>3</sub> and



the like.

#### [0013]

The composition according to the present invention is prepared by blending respective components mentioned above; resulting blended composition may be used as such for a gas generant, however, a formulated form is preferable. Any known methods are applicable for the formulation, and a suitable binder may be selected. Shape of the formulated composition is not limited specifically and may be, for example, pellet, disc, ball, like-confetti, and like-tetrapod. The formulated composition may be without holes or with holes (such as briquette with holes or ring shape).

#### [0014]

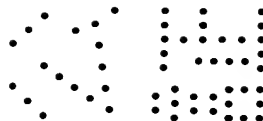
##### [Effect of the Invention]

According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, toxic components in the released gas, in particular carbon monoxide and nitrogen oxides, can be reduced to a practical level which is acceptable as an air bag system for automobile.

#### [0015]

##### [Examples]

Now, the present invention is explained more specifically concerning the first to fifth embodiments by way of examples; however,



the present invention is not limited to these examples if not out of the scope and spirit of the invention.

Hereinafter, "parts" and "%" are based on weight unless otherwise specified.

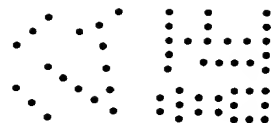
[0016]

Example 1

Powders consisting of 8 parts of DM-90 (manganese dioxide: specific surface area -  $260 \text{ m}^2/\text{g}$  (by nitrogen adsorption method)) marketed by TOYO CCI corporation, 45 parts of azodicarbonamide, 55 parts of potassium perchlorate, and 10 parts of copper oxide were blended well; furthermore, 5% aqueous solution of a soluble starch was added therewith so that the starch content be 0.55 parts. Resulting humid fine particles were adjusted to suitable fineness and water content for shape formulation, and formed into pellets ( $9.7 \text{ mm}\phi \times 4 \text{ mm}\phi$ ). The pellets were subjected to a predetermined tank test (as described in JP-B 52-3620 and JP-B 64-6156) using a burning device equipped with a filter and coolant; thereby, the concentration of carbon monoxide in the gas generated in the tank was evaluated. The burning pressure and period were of desired values. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.8% by gas chromatography. The nitrogen oxides were 1,000 ppm as determined by a gas detector tube.

[0017]





## Example 2

Example 1 was repeated except that EO8T (manganese dioxide: specific surface area - 104 m<sup>2</sup>/g (by nitrogen adsorption method)) marketed by NIKKI KAGAKU was used as the manganese dioxide. The concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank was evaluated in the same way as Example 1. The burning pressure and period were of desired values. The gas generated in the tank was found to contain 1.1% of carbon monoxide and 1,300 ppm of nitrogen oxides.

[0018]

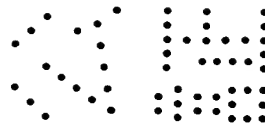
## Comparative Example 1

Example 1 was repeated except that Manganese Dioxide (manganese dioxide: specific surface area - 21.5 m<sup>2</sup>/g (by nitrogen adsorption method)) marketed by NAKARAI TESQUE, INC. was used as the manganese dioxide. The concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank was evaluated in the same way as Example 1. The burning pressure and period were of desired values. The gas generated in the tank was found to contain 2.5% of carbon monoxide and 2000 ppm of nitrogen oxides.

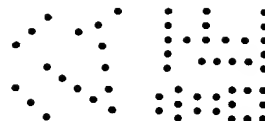
[0019]

## Example 3

Example 1 was repeated except that the amount of the manganese dioxide was increased to 10 parts. The concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank was



evaluated in the same way as Example 1-1. The burning pressure and period were of desired values. The gas generated in the tank was found to contain 0.6% of carbon monoxide and 700 ppm of nitrogen oxides.



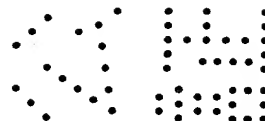
[Designation of Document] Abstract

[Abstract]

[Object] To provide a gas generant which decreases toxic components, in particular carbon monoxide and nitrogen oxides, in generated gas to a concentration practical as an air bag system for automobile.

[Structure] In the gas generant composition, a nitrogen-containing organic compound such as a compound containing amino group or amido group or a tetrazole derivative and a oxygen-containing inorganic oxidizer such as  $\text{KNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$  or  $\text{KClO}_4$  are essential components. Therewith, manganese dioxide having a specific surface area of not less than  $50 \text{ m}^2/\text{g}$  is further included.

[Selected Drawing] none



[Designation of the Document] Correction Data by Authority

[Corrected Document]

Patent Application

(Recognized and added Information)

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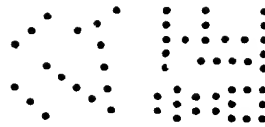
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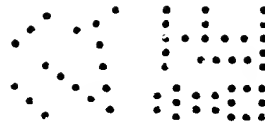
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Shinji MOCHIDA



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[Reasons of Changing]	New Registration
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